ABSTRACT

Polylactic acid (PLA) has attracted much attention due to their biodegradability and biocompatibility properties. The organically modified montmorillonite or known as nanoclay namely Cloisite B30 (the montmorillonite modified with a quaternary ammonium salt) was used in this research. PLA nanocomposite was prepared by melt intercalation method. Morphological, thermal and mechanical analysis was investigated for both pristine PLA and PLA organoclay nanocomposite. The morphological analysis was observed using both X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Thermal stability for the nanocomposites were studied using Thermogravimetric Analysis (TGA). Glass transition temperature, T_g data has been collected and analyzed using Differential Scanning Calorimeter (DSC). Other than that, the mechanical properties of the nanocomposites were observed from tensile test. From this research, a possible exfoliation of silicate layered of Cloisite B30 in the PLA matrix was demonstrated as there were no noticeable XRD peaks was observed. SEM images could not determine the nanoclay dispersion but the nanocomposite samples possessed large aggregates, whose role as stress concentrators. In thermal analysis, TGA resulted in the decrease of thermal stability with increasing loading of Cloisite B30. The glass transition temperature for the nanocomposites also has no improvement on T_g compared to pure PLA. Mechanical analysis of the nanocomposites was studied using Universal Testing Machine. A poor ultimate stress and ultimate strength but more elasticity of nanocomposites was observed compared to pure PLA.

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ABSTRAK

Asid Polilaktik (PLA) telah mendapat perhatian yang menggalakkan disebabkan oleh ciri-cirinya yang biokompabiliti dan terbiodegradasi. Montmorilonit organik yang diubah suai atau dikenali sebagai tanah liat bersaiz nano iaitu Cloisite B30 (montmorilonit yang diubah suai dengan garam ammonium) telah digunakan dalam penyelidikan ini. Nanokomposit PLA telah dihasilkan dengan menggunakan teknik interkalasi cairan. Analisis morfologi, haba dan ujian mekanikal telah dijalankan bagi kedua-dua PLA asli dan juga PLA yang telah dicampurkan dengan tanah liat bersaiz nano. Analisis morfologi telah dijalankan dengan menggunakan Pembelauan Sinar X (XRD) dan Mikroskop Imbasan Elektron (SEM). Kestabilan haba nanokomposit telah dikaji dengan menggunakan Analisis Thermogravimetri (TGA). Data suhu transisi kaca, T_g telah direkodkan dan dianalisis menggunakan Imbasan Perbezaan Kalorimeter (DSC). Selain daripada itu, ciri-ciri mekanikal yang terdapat pada nanokomposit tersebut juga telah dikaji melalui ujian tegangan. Berdasarkan kajian yang telah dijalankan, eksfoliasi silikat berlapis Cloisite B30 di dalam matriks PLA mungkin terjadi kerana tiada puncak yang ketara dapat diperhatikan daripada data yang diperolehi dari XRD. Imej SEM pula tidak dapat menentukan penyebaran bagi tanah liat bersaiz nano tetapi dapat membuktikan bahawa sampel nanokomposit mempunyai gumpalan besar yang menjadi pusat tumpuan tekanan. Dalam analisis haba, TGA mencatatkan penurunan kestabilan haba nanokomposit sejajar dengan peningkatan kandungan Cloisite B30 yang di tambah ke dalam matriks PLA. T_g bagi nanokomposit PLA juga tidak menunjukkan peningkatan jika dibandingkan dengan PLA asli. Analisis mekanikal untuk kesemua sampel telah dijalankan dengan menggunakan Mesin Ujian Universal. Tekanan maksima dan kekuatan maksima bagi nanokomposit telah merekodkan keputusan yang rendah tetapi menunjukkan ciri keelastikan yang lebih tinggi berbanding dengan PLA asli.

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LIST OF SYMBOLS

cal	Caloric
cm	Centimeter
T_c	Crystallization temperature
°C	Degree celcius
T_g	Glass transition temperature
T_m	Melting temperature
J	Joule
nm	Nanometer
s	Second
wt%	Weight percent
χ_c	Degree of crystallinity
θ	Theta

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LIST OF ABBREVIATIONS

Al	Aluminum
ASTM	American Society for Testing and Materials
CEC	Cation exchange capacity
CNT	Carbon nanotube
DSC	Differential Scanning Calorimeter
EPMgMA	Maleic anhydeide-grafed ethylene propylene rubber
LDH	Layered double hydroxide
LLDPE	Linear low density polyethylene
MSF	Modified soy flour
MWCNT	Multi-wall carbon nanotube
OMMT	Organo-montmorillonite
PEG	Polyethylene glycol
PLA	Polylactic Acid
SEM	Scanning Electron Microscopy
SF	Soy flour
SWCNT	Single-wall carbon nanotube
TEM	Transmission electron microscopy
TGA	Thermogravimetric Analysis
TPO	Thermoplastic polyolefin
WD	Wood floor
XRD	X-ray Diffraction

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CHAPTER ONE

INTRODUCTION

1.1. BACKGROUND OF RESEARCH

Polymer is a large molecule that is macromolecule which made up from repeating structural units typically linked by covalent chemical bonds. The first polymer used was natural products, especially cotton, starch, proteins, and wool. Polymer refers to a large class of natural and synthetic materials with a wide variety of properties. The wide application of polymer is in plastic industry. Due to the extraordinary range of properties of polymeric materials, polymer plays an essential role in everyday life, ranging from familiar synthetic plastics and elastomers to natural biopolymers such as DNA and proteins.

Nanotechnology is now recognized as one of the most promising areas for technological development currently. Nanotechnology can be defined as the science and engineering in the design, synthesis, characterization, and application of materials and devices where the smallest dimension of particles is on the nanometer scale or one billionth of a meter (Kamel, 2007). In materials research, the development of polymer nanocomposites is rapidly emerging as a research activity that could broaden the applications of polymers for the benefit of many different industries. Polymer nanocomposites are polymers which are thermoplastics, thermosets or elastomers that have been reinforced with small quantities.

Nanoscale interactions have significant implications on the macroscopic behaviour of materials as every structural level contributes to the mechanical stability and durability of the resulting materials (Ciprari, 2004). It has become increasingly

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important to understand and manipulate materials at the nanoscale to develop new functional materials for engineering and other application. Nanostructured and nanocomposite materials can show significant improvement of mechanical properties (Khudyakov, David Zopf & Turro, 2009).

Polylactic acid (PLA) is a biodegradable polymer derived from a lactic acid. It is a highly versatile material which made from 100% renewable resources such as corn, sugar beet, wheat and other starch-right products. It exhibits many properties that are comparable to or better than many petroleum based plastics that make PLA can be use for various applications (Platt, 2006). PLA cannot be considered as a new biodegradable polymer because as early as 1845, it was synthesized by Theophile-Jules Pelouze by the condensation of lactic acid (Auras *et. al.*, 2010). Figure 1.1 shows the classification of biodegrable polymer.

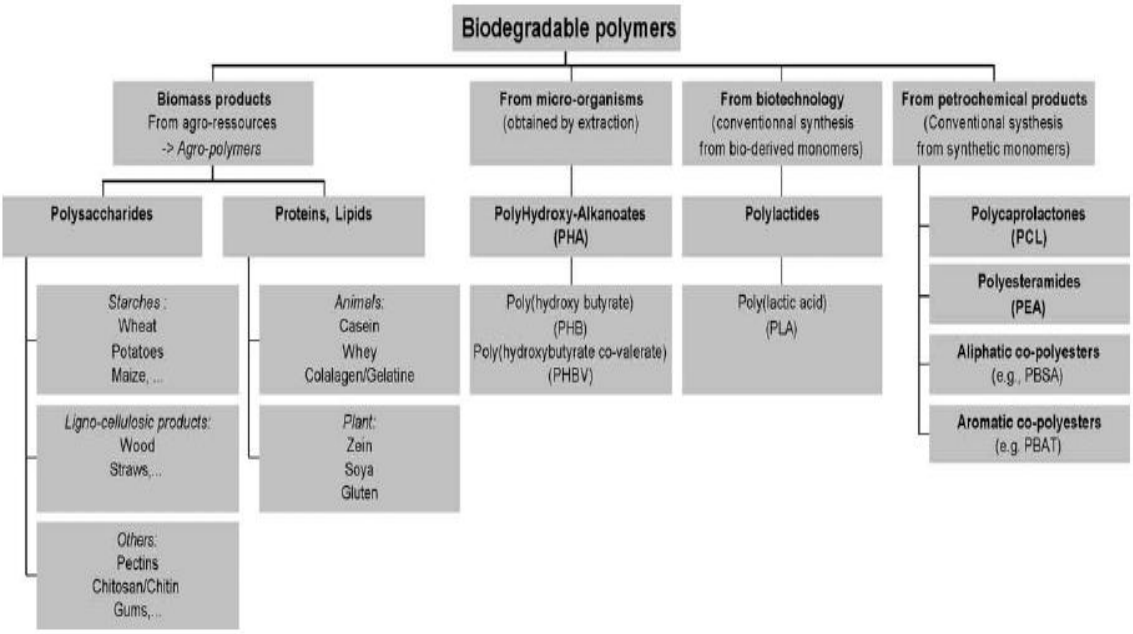

Figure 1.1: Classification of the biodegradable polymers

Source: Averous and Boquillon (2004)

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Polymer composite theory predicts that improved bonding between polymer and matrix leads to improved mechanical properties. Despite these predictions, however, mechanical testing of nanocomposites has shown mixed results. Some experimental data has shown that reduced particle size improves mechanical properties, specifically elastic modulus. Other studies have shown that elastic modulus decreases with reducing on dimension (Ciprari, 2004).

In the past decade, extensive research has focused on polymer nanocomposites in hopes of exploiting the unique properties of materials in the nano-sized particle. A general conclusion has been drawn that nanocomposites show much improved mechanical properties over their micro-sized counterparts. Because of their small size, nanoparticles have a high surface to volume ratio and provide high energy surfaces (Winey, 2006). An expected result of embedding nanoparticles into a polymer matrix is enhanced bonding between the polymer matrix and filler, resulting from the nanoparticles' high interfacial energy (Li *et. al*., 2010).

1.2 PROBLEM STATEMENT

PLA composite (microcomposite) is traditionally used in industries but it offers low strength and low thermal stability of material. Therefore, PLA nanocomposite is introduced because it shows improvement in those properties.

1.3 RESEARCH OBJECTIVE

1.3.1 To investigate the thermal properties of PLA nanocomposite that is incorporated with modified nanoclay.

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1.4 SCOPE OF RESEARCH

This research is focusing on PLA nanocomposites which is biodegradable aliphatic polyester that can be synthesize from renewable resources. The scopes of this research are as follow:

1.4.1 Cloisite B30 is type of nanoclay known as montmorillonite modified with a quaternary ammonium salt was used as nanofiller in this research that is to be incorporated with pristine PLA. Nanoclay is chosen as the nanofiller because it is easy to acquire from suppliers and the price is low compared to other nanofiller such as carbon nanotube (CNT).

1.4.2 Melt intercalation method is implemented to prepare PLA nanocomposite as it is widely use in industrial application.

1.4.3 Characterization of PLA nanocomposite consists of morphological and thermal analysis. The morphological analysis was done using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). In addition, Differential Scanning Calorimeter (DSC) and Thermogravimetric Analysis (TGA) have been utilized in order to observe the thermal behaviour of PLA nanocomposites.

1.4.4 The mechanical properties of the nanocomposites was obtained from tensile test result.

1.5 SIGNIFICANCE OF RESEARCH

This research discussed about virgin PLA that was incorporated with Cloisite B30 forming PLA nanocomposite as the key of modification. Polymer nanocomposites consisting of a polymer matrix with nanoparticle filler, have been predicted to be one of the most beneficial applications of nanotechnology. Nanoparticles provide better thermal and mechanical properties compared to microparticle. PLA nanocomposite is one of the most promising biodegradable polymer as it can be produce from 100% renewable resources. It is relatively cheap and has some remarkable properties that it

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suitable for different applications. Besides, PLA has been intensively studied and used for biomedical material as it can be degraded in human body. The use of PLA has been further extended for food packaging applications because of its high film and packaging performance characteristics. Currently, PLA is used for containers for bottled water packaging, bottled juices, sandwich containers, and yogurts (Ahmed, Varhney, & Auras, 2010).

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CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

Nanotechnology is one of the most popular fields for research and development currently. The term 'nanotechnology' is only specifically referred recently although nanotechnology involve nanoscale dimension has been discovered decades ago. Nanoscale interactions have profound implications on the macroscopic behaviour of materials as every structural level contributes to the mechanical stability and durability of the resulting materials (Devaprakasam *et. al.*, 2007). In nanocomposite field with the critical scale below 100nm, there are many diverse topics which consist of composite reinforcement, barrier properties, flame resistance, electro-optical properties, cosmetic applications, bactericidal properties. This review will focus on polymer nanocomposite, types of nanocomposites, PLA composite, PLA nanocomposite and a characterization method of nanocomposite.

2.2 POLYMER NANOCOMPOSITE

A polymer composite is a combination of a polymer matrix and a strong reinforcing phase, or filler. Polymer composites provide desirable properties unavailable in matrix or filler materials alone. A polymer nanocomposite is a polymer matrix with a reinforcing phase containing one dimensional nano-sized particle. Nanocomposites are polymers with particle-filled which at least one dimension of the dispersed particle is in nanometer scale (Kashiwagi *et. al.*, 2004). The polymer nanocomposites also defined as polymer matrix containing nanostructures of inorganic nature (Fréchette & Reed, 2007).

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In order to enhance the performance of polymer especially rubber, fillers of polymers is introduced. According to Ciprari's studies, 2004 nanocomposites showed improvements in mechanical properties over their micro-sized similar systems. It is due to nanoparticles have a high surface to volume ratio and provide high energy surfaces. Polymer composite theory suggests that improved bonding between polymer and matrix leads to improved mechanical properties.

Besides that, increase of polymer toughness (J/m^3) always considered as an improvement or enhancement of polymer nanocomposites properties (Kudyakov et al., 2009). In addition, polymers with nanoscale additive showed an improvement in flammability properties because one weak aspect of polymer is that they are combustible under certain conditions but nanocomposites provide a possible alternative to conventional flame retardants (Kashiwagi *et. al*., 2004).

Devaprakasam *et. al*., studies state that nanoparticles with uniform packing density in the polymer matrix results in homogeneous mechanical properties compared to microcomposite which results in heterogeneous mechanical properties. It is due to high energy dissipation and big particles with weak interfacial bonding of microcomposite. The clay-based nanocomposites always obey continuum mechanics predictions where they can exhibit properties not expected with larger scale particulate reinforcemens (Paul & Robeson, 2008). The wear resistance of the nanocomposite is enhanced as the strong interfacial bonding between the nanoparticles and matrix due to high specific area of nanoparticle. Thus, it offers better nanotribo-mechanical performance compared to that of the microcomposite (Devprakasan *et. al.*, 2007).

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Table 2.1 Example of nanocomposites commercial utility

Polymer Matrix	Nanoparticle	Property improvement	Application
Polyamide 6	Exfoliated clay	Stiffness	Timing belt cover for automotive
Thermoplastic polyolefin (TPO)	Exfoliated clay	Stiffness and strength	Exterior step assist
Epoxy	Carbon nanotubes	Stiffness and strength	Tennis rackets
Epoxy	Carbon nanotubes	Stiffness and strength	Hockey sticks
Polyisobutylene	Exfoliated clay	Permeability barrier	Tennis balls, tires and soccer balls
SBR, natural rubber and polybutadiene	Carbon black (20-100 nm: primary particles)	Strength and wear	Tire
Various	MWCNT	Electrical conductivity	Electrostatic dissipation
Unknown	Silver	Antimicrobial	Wound care and bandage
Nylon MXD6, PP	Exfoliated clay	Barrier	Beverage containers and film
SBR rubber	Not disclosed	Improved tire performance in winter	Winter tires
Natural rubber	Silver	Antimicrobial	Latex gloves
Various	Silica	Viscosity control and thixotropic agent	Various
Polyamides nylon 6, 66, 12	Exfoliated clay	Barrier	Auto fuel system

Source: Paul and Robesson, (2008)

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2.3 TYPES OF NANOCOMPOSITE

Nanoparticles are classified in three different natures. The types of nanocomposite comprising of intercalated clay, exfoliated clay and phase separated polymer-nanocomposite. From the three nanocomposites, exfoliated clay is the most desired one. The three main types of nanocomposite are schematically presented in Figure 2.1.

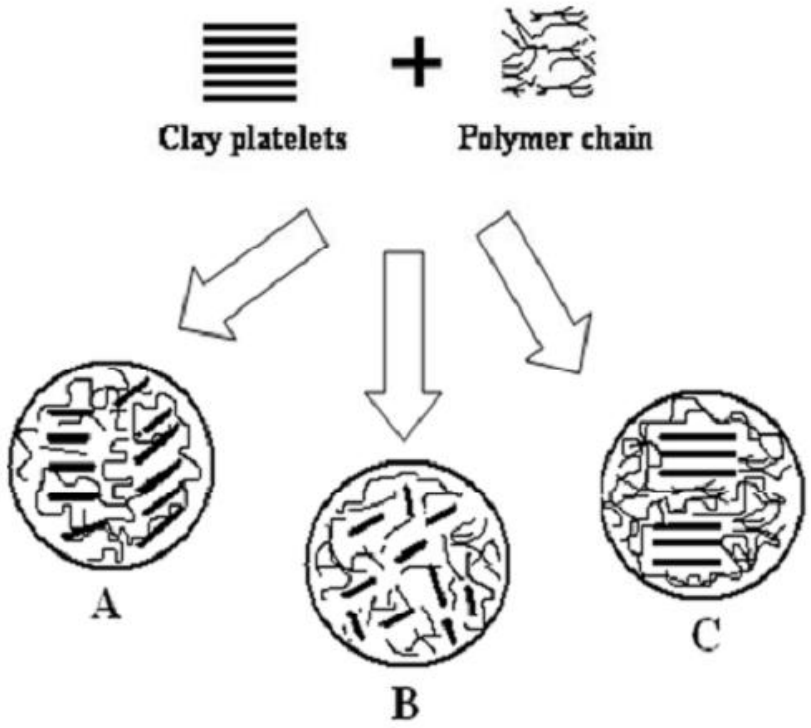

Figure 2.1: Schematic of the (A) intercalated, (B) exfoliated structure and (C) phase separated of polymer nanoclay composite morphology

Source: Bhat. *et. al*. (2008)

2.3.1 Exfoliated Nanocomposites

Exfoliation is a measure of how separated the nanoclay platelets are (Snyder, 2007). Complete exfoliation that is separation of platelets from one another and dispersed individually in the polymer matrix is the desired goal of formation for many

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purposes. Paul and Robesson studies have suggested alternative ideas about how the details of the mixing equipments and conditions change the state of the dispersion achieved. The ideas are summarized in the figure below:

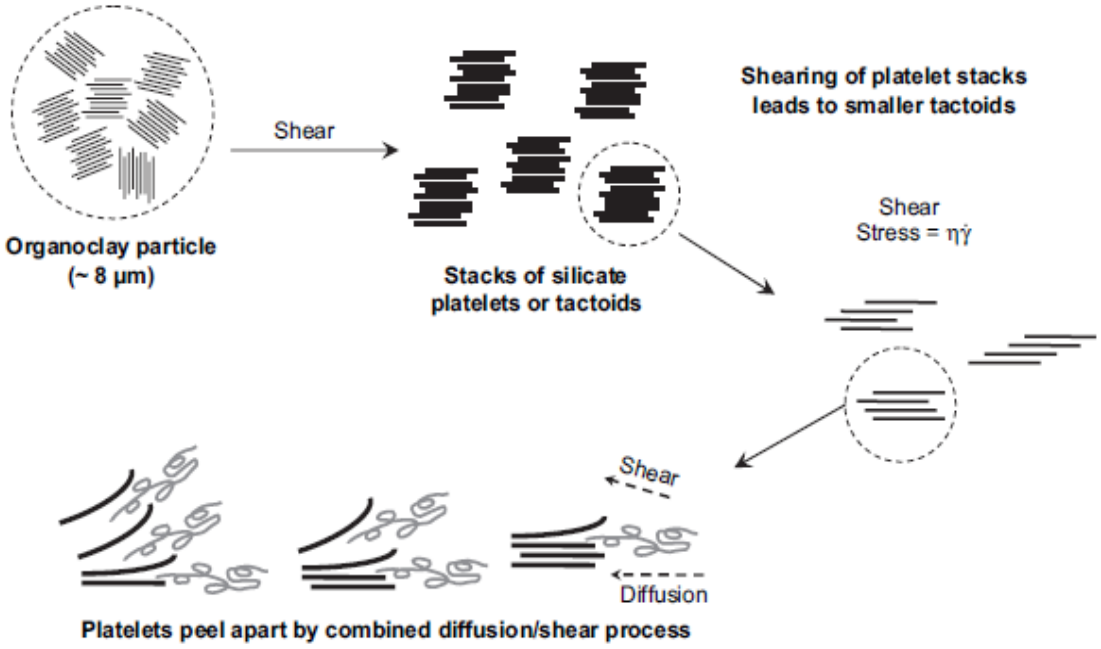

Figure 2.2: Mechanism of organoclay and exfoliation during melt processing

Source: Paul and Robeson (2008)

Comparing to the pristine polymer or polymer with smectic clay, exfoliated nanocomposite with high aspect ratio demonstrates enhance properties and in most cases (Kudyakov *et. al*., 2009). Based on modification of polymeric systems, exfoliated clays could result in significant mechanical property advantages (Gacitua, Ballerini & Zhang, 2005). In intercalated nanocomposites, the unit cells of clay structure are expended by the insertion of polymer into the interlayer spacing while the periodicity of the clay structure is maintained. However, the crystal structure of the clay for exfoliated nanocomposite is completely exfoliated by individual dispersion of the clay layers into the polymer matrix (Yusoh, Jin & Song, 2010). The difference in the micro-phase morphology of these two types is the reason in the difference of their physical properties (Xia, Shaw & Song, 2005). There is a number of ways to increase a degree of

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exfoliation in a nanocomposite, such as in situ polymerization, melt blending, solution blending, sonication, high shear mixing, melt intercalation (Kudyakov et al., 2009).

2.4 NANOCLAY

Montmorillonite or also known as clay consist of platelets with an inner octahedral layer sandwiched between two silicate tetrahedral layers as illustrated in Figure 2.3. It is the most widely used clay to prepare polymer nanocomposites. The dioctahedral 2:1 phyllosilicate consists of silica tetrahedrons having oxygen and hydroxyl ions tetrahedrally arranged around Si atom. The base of the tetrahedrons is made up of oxygen atoms while the hydroxyl group makes up the tip of the tetrahedron and is fused with the aluminum octahedron (Alian, 2008).

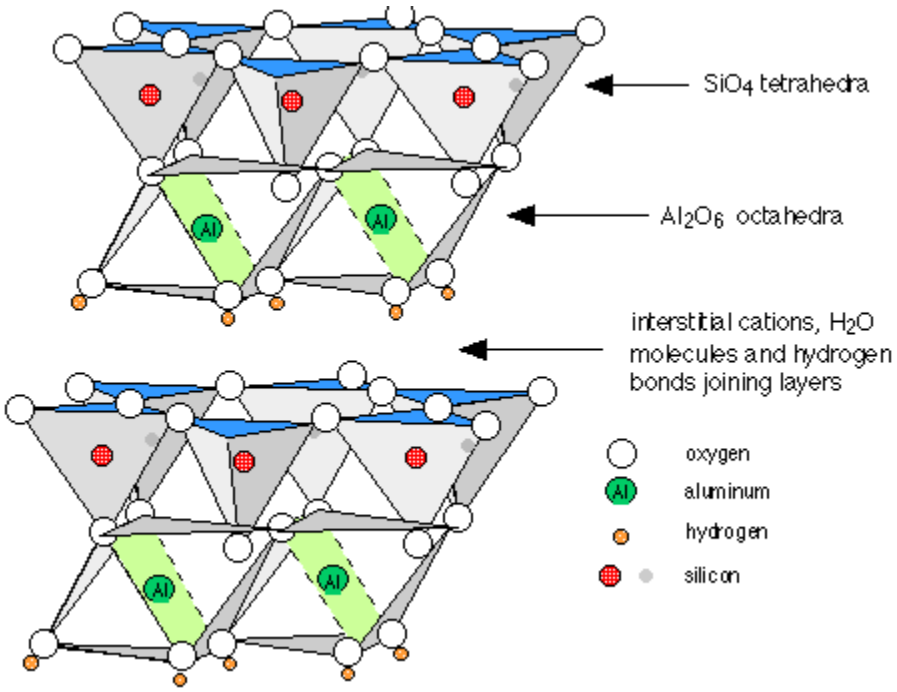

Figure 2.3: Structure of montmorillonite

Source: Galgali (2003)

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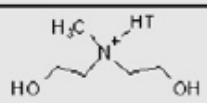
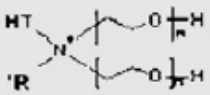
Filler in the nanoscale is known as nanoclay. A valuable nanocomposite is one with the largest possible surface of nanofiller. In fact, it means avoiding aggregation of nanoparticles but exfoliation of nanoclays is the most desired type of nanocomposite (Kudyakov *et. al*., 2009). Nanoclay is a type of filler which is one of the most affordable materials in industry. It is made of montmorillonite mineral deposits that known to have platelets structure with average dimension of 1 nm thick and 70 to 150 nm wide (Bhat, Hegde, Kamath, & Deshpande, 2008). A measure of how thoroughly mixed a clay with a resin is called dispersion.

A technique that is used to analyze the dispersion is by examining the location where there is no nanoclay present as to determine whether the clay is evenly distributed among the resin. However, exfoliation is a measure of how separate nanoclay platelets are. The analysis technique of exfoliation is an attempt to determine the average spacing between platelets. The analysis is also to quantify the number of platelets in each particle. While there is currently no single system that can describe both the levels of exfoliation and dispersion of the nanoclays with complete certainty, X-ray Diffraction (XRD) coupled with Transmission Electron Microscopy (TEM) microscope analysis is the most reliable and is currently the most often used to examine clay containing nanocomposites (Ryan, 2007).

Table 2.2: Characteristics of clay

Type of clay	Commercial name	Modifier structure	Code
Montmorillonite	CLOISITE 30B		CLO30B
Montmorillonite	NANOFIL 804	 (n~1)	NAN804
Sepiolite	PANGEL S9	none	SEPS9

Source: Fukushima, Tabuani, and Camino (2008)

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